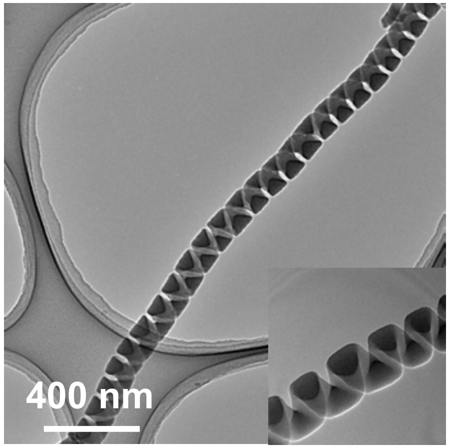
Synthesis, Characterization, and Manipulation of Helical SiO_2 Nanosprings

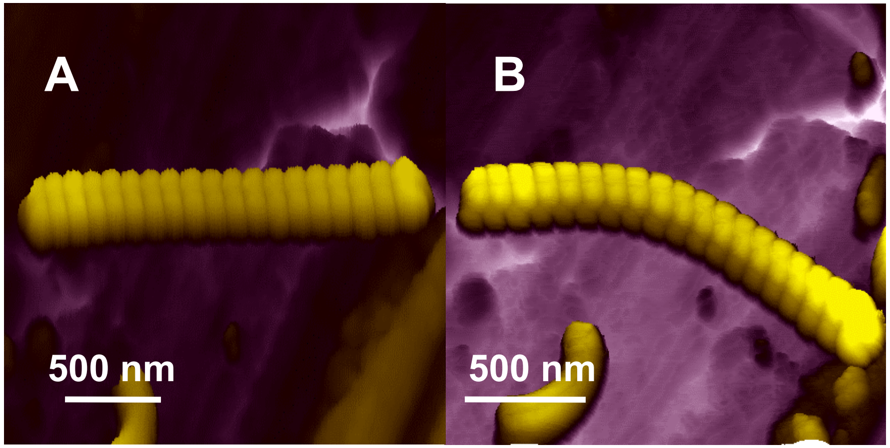
Lai-Sheng Wang, Washington State University, DMR-0095828

Helical nanosprings represent a new variety among the family of one-dimensional nanostructures, which have attracted great attention in nanoscience recently. In addition to their structural flexibility, nanosprings present opportunities for nano-engineering, such as helicity and periodicity. We synthesized amorphous helical SiO_2 nanosprings (80 to 140 nm in diameter and up to 8 micron long) for the first time and characterized them by scanning and transmission electron microscopy (TEM) and atomic force microscopy (AFM). Contraction and expansion of the helical nanosprings were observed under in situ electron beam heating during TEM, as well as bending induced by an AFM tip, suggesting that the helical nanosprings are highly flexible and may have potential applications in nanomechanical, nanoelectromagnetic devices, and composite materials.

Nano Lett. **3**, 577-580 (2003).



TEM image of an amorphous SiO_2 nanosping. The inset shows a higher resolution image of the nanosping.



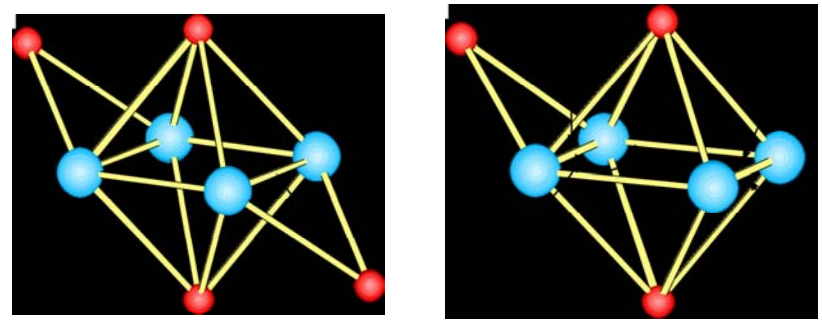
Manipulation of the silica nanospring by AFM. (A) before and (B) after the manipulation, showing its flexibility and elasticity.

All-Metal Antiaromatic Molecule: Rectangular Al_4^{4-} in the $Li_3Al_4^{4-}$ Anion

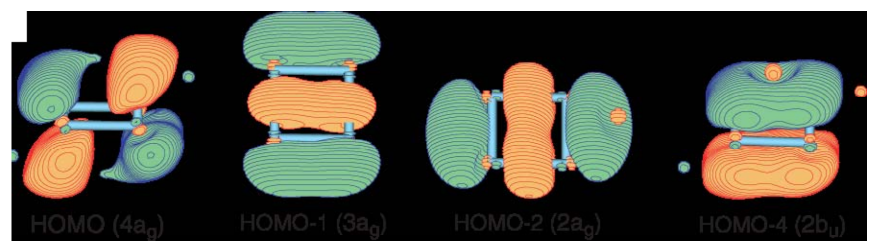
Lai-Sheng Wang, Washington State University, DMR-0095828

Aromaticity and antiaromaticity are two important concepts in organic chemistry. Aromatic molecules contain $4n + 2$ π electrons and have special structural and electronic stability. Antiaromatic molecules contain $4n$ π electrons and have characteristic structural distortions and electronic instability. We previously discovered the first all-metal aromatic molecule, Al_4^{2-}. Here we present the discovery of an all-metal antiaromatic molecule, Al_4^{4-} in $Li_3Al_4^-$. Experimental and theoretical evidence shows that the most stable structure of $Li_3Al_4^-$ contains a rectangular Al_4^{4-} interacting with three Li^+ ions. Molecular orbital analyses reveal that the rectangular Al_4^{4-} has four π electrons, consistent with the $4n$ Huckel rule for antiaromaticity. This finding completes extension of two important chemical concepts, aromaticity and antiaromaticity, into the realm of metallic systems and may help understand properties of bulk metallic and intermetallic systems.

Science **300**, 622-625 (2003).



The optimized structures of Li_4Al_4 and $Li_3Al_4^-$ (Li: red; Al: light blue), showing the rectangular Al_4 unit. The rectangular shape, rather than a square shape, is due to antiaromaticity in the Al_4^{4-} unit.



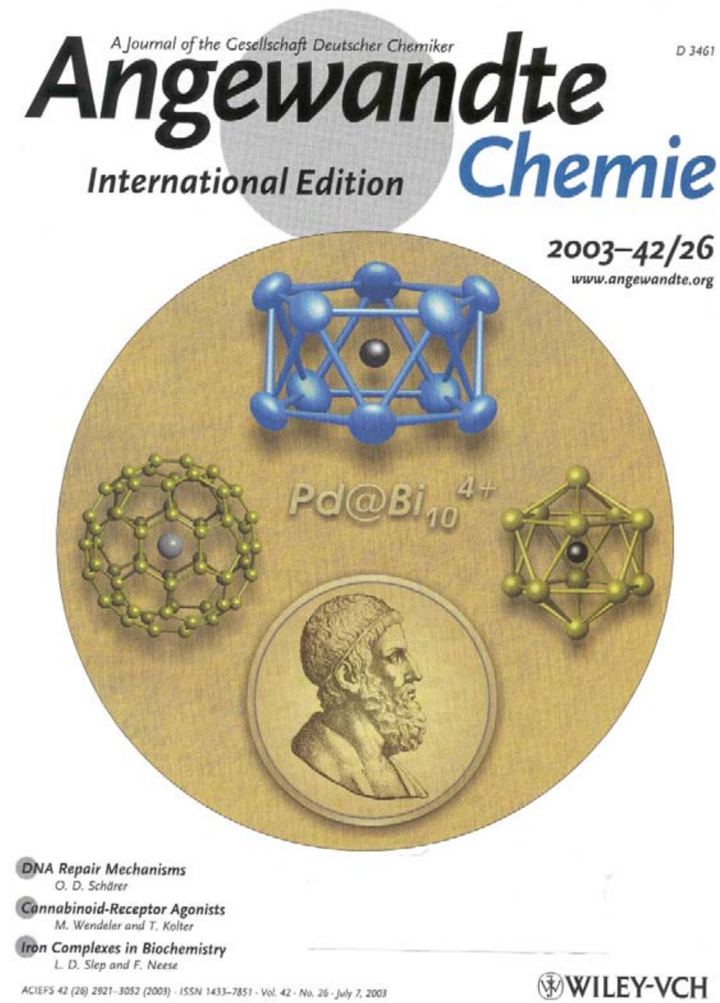
The occupied valence molecular orbitals of Al_4^{4-}. The HOMO and HOMO-4 are the two π orbitals responsible for the antiaromaticity.

Observation and Confirmation of Icosahedral $W@Au_{12}$ and $Mo@Au_{12}$ Molecules

Lai-Sheng Wang, Washington State University, DMR-0095828

One of the major goals of cluster science is to discover highly stable clusters, which may be used as building blocks for novel nanomaterials, such as the celebrated C_{60}. A remarkable series of highly stable and symmetric clusters were predicted that contain 12 Au atoms with an encapsulated central impurity atom of the 5d elements, $M@Au_{12}$ ($M = W, Ta^-, Re^+$).   We first observed and characterized the icosahedral $W@Au_{12}$ cluster using photoelectron spectroscopy and relativistic density functional calculations. In addition, we also observed and characterized $Mo@Au_{12}$, which were shown to have identical structure and properties as $W@Au_{12}$. The experimental observation and confirmation of the stable endohedral clusters paved the way for their eventual bulk synthesis.

Angew. Chem. Int. Ed. **41**, 4786 (2002).



Cover of *Angew. Chem. Int. Ed.* featuring (clockwise) $He@C_{60}$, $Pd@[Bi_{10}]^{4+}$, $W@Au_{12}$, and Archimedes, who first described the polyhedron characteristic of $Pd@[Bi_{10}]^{4+}$.

Experimental Investigation of Aluminum-Alloy and Metal Carbide Clusters: From Gas Phase Studies to Syntheses of Cluster-Based Nanomateirals

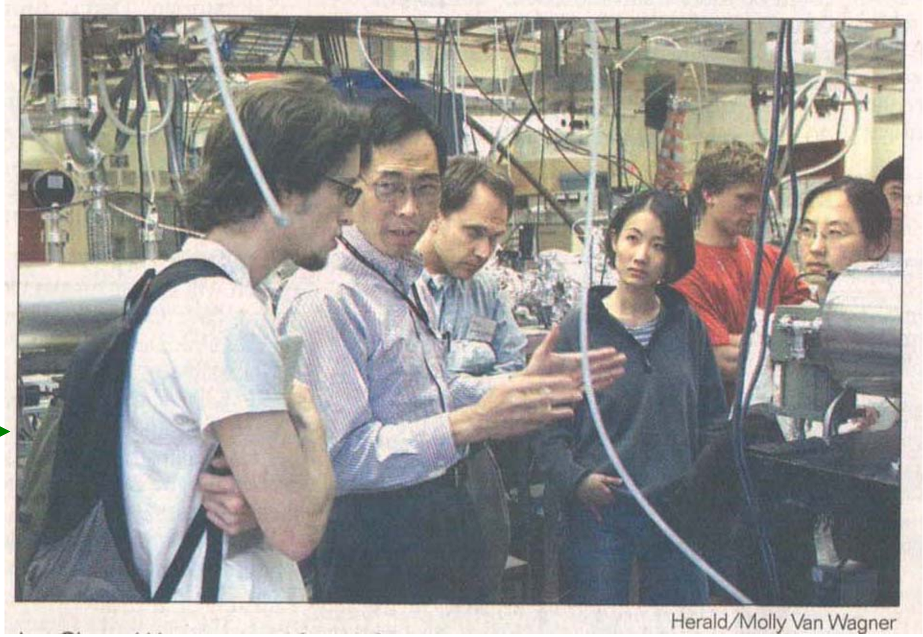
Lai-Sheng Wang, Washington State University, DMR-0095828

Education:

One graduate student (Xi Li) and two postdoctoral fellows (H. F. Zhang and H. J. Zhai) have contributed to the experimental work. There is a major theoretical collaboration with Prof. Boldyrev's group from Utah State University. Two undergraduate students (N. A. Cannon and K. A. Birch) and two graduate students (A. E. Kuzbetsov and A. N. Alexandrova) from USU have contributed to the theoretical work.

Curriculum Development:

A new course, Phys. 581: Nanoclusters, Nanomaterials, and Nanotechnology, was developed partly based on research supported by this grant. Research results from this grant, as well as the PI's research equipment, were integrated into the course.



Students from the Phys. 581 course listening to Prof. Wang in his research lab and learning about cluster generation and photoelectron spectroscopy. This picture appeared in the Tri-City Herald on its May 26, 2003 edition along with an article titled "Nanoscience class one of few" about the Phys. 581 course given on-site at PNNL from May 19-30, 2003.